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CRADA Final Report
For
CRADA Number ORNL98-0518

WAX POINT DETERMINATIONS USING
ACOUSTIC RESONANCE SPECTROSCOPY

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ABSTRACT

The thermodynamic characterization of the wax point of a given crude is essential in order to maintain flow conditions that prevent plugging of undersea pipelines. This report summarizes the efforts made towards applying an Acoustic Cavity Resonance Spectrometer (ACRS) to the determination of pressures and temperatures at which wax precipitates from crude. Phillips Petroleum Company, Inc., the CRADA participant, supplied the ACRS. The instrumentation was shipped to Dr. Thomas Schmidt of ORNL, the CRADA contractor, in May 2000 after preliminary software development performed under the guidance of Dr. Samuel Colgate and Dr. Evan House of the University of Florida, Gainesville, Fl. Upon receipt it became apparent that a number of modifications still needed to be made before the ACRS could be precisely and safely used for wax point measurements. This report reviews the sequence of alterations made to the ACRS, as well as defines the possible applications of the instrumentation once the modifications have been completed.

1. OBJECTIVES

The purpose of this Cooperative Research and Development Agreement (CRADA) between Phillips Petroleum Company, Inc. (Participant) and Lockheed Martin Energy Research Corporation (Contractor) was the measurement of the formation of solids in crude oils and petroleum products that are commonly transported through pipelines. This information is essential in the proper design, operation and maintenance of the petroleum pipeline system in the United States. Recently, new petroleum discoveries in the Gulf of Mexico have shown that there is a potential for plugging of undersea pipeline because of the precipitation of wax. It is important that the wax points of the expected crude oils be well characterized so that the production facilities for these new wells are capable of properly transporting the expected production.

The goal of this work is to perform measurements of solids formation in crude oils and petroleum products supplied by the Participant. It is anticipated that these data will be used in the design of new production facilities and in the development of thermodynamic models that describe the behavior of wax-saturated petroleum.

2. BENEFITS TO THE MISSION OF THE DOE FUNDING OFFICE

This project will provide a new technology at ORNL for the determination of critical physical and chemical data on gases, liquids, and solids found in the petroleum and chemical industries. It will provide those within DOE's Fossil Energy program, as well as Phillips Petroleum Company, with data related to wax point deposition from petroleum fluids.

3. DISCUSSION OF WORK PERFORMED

The tasks defined in the original scope of work cited in the CRADA were:

1. Modify the equipment to meet the expected experimental needs at ORNL. The modifications were to be carried out under the supervision of ORNL personnel. Completion was expected by June 1, 1998.

2. The selection of the fluid systems to be studied was to be made by joint agreement between ORNL and Phillips Petroleum Company. Completion was expected by September 30, 2000.
3. Measurement of wax point using the Acoustic Cavity Resonance Spectrometer (ACRS) was to be conducted jointly. Equipment responsibility would be with ORNL. Phillips staff was to advise on the experimental conditions and was to supply the fluids for the study. Completion was expected by September 30, 2000.

As a preliminary task, the ACRS and its associated equipment had to be transferred from Phillips Petroleum Company to ORNL. At the initiation of the CRADA the ACRS was being upgraded at the University of Florida at Gainesville under the supervision of Dr. Samuel O. Colgate. Phillips was funding Dr. Colgate to modernize the software that provided instrument control and data acquisition for the ACRS. Dr. Evan House, an electrical engineer and former graduate student of Dr. Colgate, assumed the responsibility to alter the control architecture such that a single computer would control the operation of the ACRS. Using LabVIEW programming software, his goal was to manage the operation of the various mechanical and electrical components such that frequency data arrays could be acquired by either continuously altering the volume of the cavity or temperature of the oven.

The development of the control software was at a point by October of 1999 that Dr. Leon N. Klatt of ORNL traveled to Gainesville, Florida, to view the operation of the modified ACRS. Dr. Klatt made several recommendations to improve the data quality under the new LabVIEW programming. It was his opinion that the major reason for the poor quality of the acoustic efficiency at pressures below the bubble point was that the data were acquired while the cavity volume was actually being swept. He believed that, with the precision in the data that would be needed for wax point determinations, this was not the way to acquire these data. Some of the reasons for this opinion were:

- (1) the quality of the acoustic data can be decreased when it is acquired while the piston position is changing because vibrations from the piston drive system can be coupled to the acoustic detector,
- (2) acquiring the acoustic data as the volume is being swept eliminates the possibility of performing signal averaging to improve the quality of the raw data,
- (3) the density change during the data acquisition is assumed to be negligible, and
- (4) acquiring the acoustic data while the volume is changing assumes that the equilibrium between the liquid and gas phase are achieved instantaneously.

Dr. Klatt suggested that the acquisition of bubble point data be performed using a step volume scan technique—adjust the volume and then measure the acoustic efficiency followed by the next volume change and another acoustic efficiency measurement. This approach would address all of the concerns noted above.

To accommodate these suggestions, Dr. House modified the program such that frequency data would be acquired only when the piston was stationary. In February 2000,

Debra Bostick of ORNL met with Dr. House in Gainesville to be trained in the operation of the ACRS as it was configured at that time. A preliminary operating manual was written based on the notes taken from this meeting. This manual provided the only written documentation of the system that was subsequently shipped to ORNL in May 2000.

As can be inferred from the preliminary operating manual, a number of modifications still needed to be made before the ACRS could be precisely and safely used for wax point measurements. Required additions to the system included:

- (1) Software programming needed to be incorporated that would control the operation of a needle valve used to introduce liquid nitrogen into the ACRS oven. Such a system was to have allowed controlled cooling of the cavity such that frequency data could be acquired at temperatures as low as -20°C .
- (2) Manual control of the stepping motor used to drive the piston did not operate consistently. The manual switch on the control panel did not work at all settings. The circuit board driving the stepping motor would occasionally introduce excessive electrical noise into the frequency response of the cavity.
- (3) The ARS oven is equipped with a large piston located within the base of the oven unit. A double-action pneumatic air valve, operated through the parallel port of the computer, controls the piston movement. The purpose of the piston is to provide mixing of the contents of the ACRS cavity prior to a data run. The control of the valve needed to be incorporated into the programming software. A single line of the computer parallel port was to be used with a 0.1-0.2 Hz/5 sec signal. The computer address of the parallel port was not provided at the time of delivery so that this programming could be accomplished.
- (4) Three pressure gauges were to be supplied to cover the operating ranges of 0-2000 psi; 0-15 psi is also available. A 0-500 psi gauge was not received with the system.
- (5) Of greatest concern from a safety standpoint was that there was no logic programming written to automatically shut down the ACRS system if heating of the contents of the cavity caused a rapid pressurization of the system. This was to be done manually by the operator by opening the oven door to rapidly cool the system. The operator was then to turn off the computer so that the temperature PID control loop was cut off. A second safety concern was presented if the computer power flickered or turned off, or if the computer programming locked up. Under these conditions there would be no logic control of oven heating. The temperature limit for the piezoelectric transducers is 150°C . Therefore, the oven power needed to be turned off manually to prevent transducer damage and over-pressurization until computer control of the system could be reinstated.

A summer student intern was hired in May 2001 through the DOE Energy Research Undergraduate Laboratory Fellowship program to begin making the required modifications. Carl Willis (Guilford College, Greensboro, NC) improved the

temperature control of the system. Having received no documentation of the LabVIEW program from the University of Florida, Mr. Willis was still able to revise the programming to create two separate temperature routines—one for heating, the other for cooling. While performing this task it became apparent that the mechanism originally devised for the cooling of the ACRS would not be adequate to operate the system below 0°C. The cooling mechanism would have to be reengineered, based on a refrigeration unit, to adequately and uniformly chill the ACRS. The revised heating program controlled the operating temperature to within 0.01 °C. The temperature ratings for various instrument components were also determined through a literature search. The upper temperature limit is set by the temperature sensitivity of the piezoelectric transducers and the gaskets incorporated within the sample cavity. Thus, the useful operating temperature was determined to be 0-110 °C. As a final activity Mr. Willis attempted to calibrate the volume and pressure transducers. Accurate volume calibration was achieved. However, it became obvious that the cavity and associated transfer lines had numerous leaks. At the end of his tenure Mr. Willis amended the operating instructions (Attachment B) for the system to summarize his alterations in the LabVIEW control program and to document suggested modifications that he believed were needed for successful use of the ACRS.

Alterations of the ACRS are still in progress. Dr. Robert Gavriluc, an associate professor at the Faculty for Building Services Engineering Bucharest (Romania), Department of Thermodynamics, is currently assessing the status of the ACRS under a scholarship of the Fulbright Foundation. His intended research plan was to determine the thermodynamic parameters (c_v , c_p , and c_{JT}) of dimethyl ether using the ACRS. (A project statement for his work is included in this report as Attachment C.) Dr. Gavriluc is meticulously reviewing the hardware and software parameters of the system to verify the accuracy of the equipment. Thus far, he has had to alter the LabVIEW program to correctly define the frequency response. Additionally, he has corrected an error in the calibration equation for determining the temperature from the analog signal of the platinum resistance thermometer. He is currently attempting to eliminate gas leaks in the system so that he can define the temperature sensitivity of the pressure transducer.

With better familiarity of the ACRS unit, it has become apparent that Dr. Gavriluc must modify his scope of work to account for the limitations in the current setup of the ACRS. A majority of his efforts will concentrate on calibration of the system, as is, so that others in the future will be able determine thermodynamic constants of systems over a limited operating range.

The ability to determine wax points of petrochemical samples can be improved. System requirements under conditions similar to that of undersea pipelines are such that data must be acquired within a temperature range of +90 to -4 °C. The refrigeration system for the ACRS would have to be designed to accomplish this degree of cooling. Additionally, the piezoelectric transducers would have to be interchanged with components rated for low-temperature applications. Nominal pressure in the pipeline is 10 bar (145 psi). This pressure range is achievable provided that transfer lines, valves, and seals are reconditioned or replaced. As the system currently exists, the fact that

petroleum samples were never received from Phillips Petroleum Company is somewhat mute. Further development will be required before wax point determinations can be made.

For the ACRS to be applicable to samples of general interest in the petrochemical industry, the system would have to be further modified. The operating range of the unit will need to cover near-liquid nitrogen temperatures through 300 °C. The cavity most probably would have to be redesigned to withstand high-end pressures of 5000 psi. Finally, additional safety controls should be added to circumvent the possibility of loss of computer control and inadvertent pressure spikes. Once accomplished, acoustic measurement of samples parameters could provide a highly accurate, useful tool for petrochemical characterization.

APPENDIX A

ACOUSTIC RESONANCE SPECTROMETER (ARS) OPERATING NOTES

Acoustic Resonance Spectrometer (ARS) Operating Notes

ARS Operating Principle

The ARS is designed to measure the speed of sound in a media of interest under controlled conditions of temperature and pressure. The device used an 8-mL cylindrical resonant cavity. A piezoelectrical transducer at the top of the cylinder introduces an acoustic wave into the media; the transmitted time-domain signal intensity is detected with a second piezoelectric transducer located at the base of the cavity. The detected signal is transformed to the frequency domain. The frequency of the acoustic wave is scanned and correlated with pressure and/or temperature to determine various physical properties of the sample matrix.

Instrument Panel Set-Up

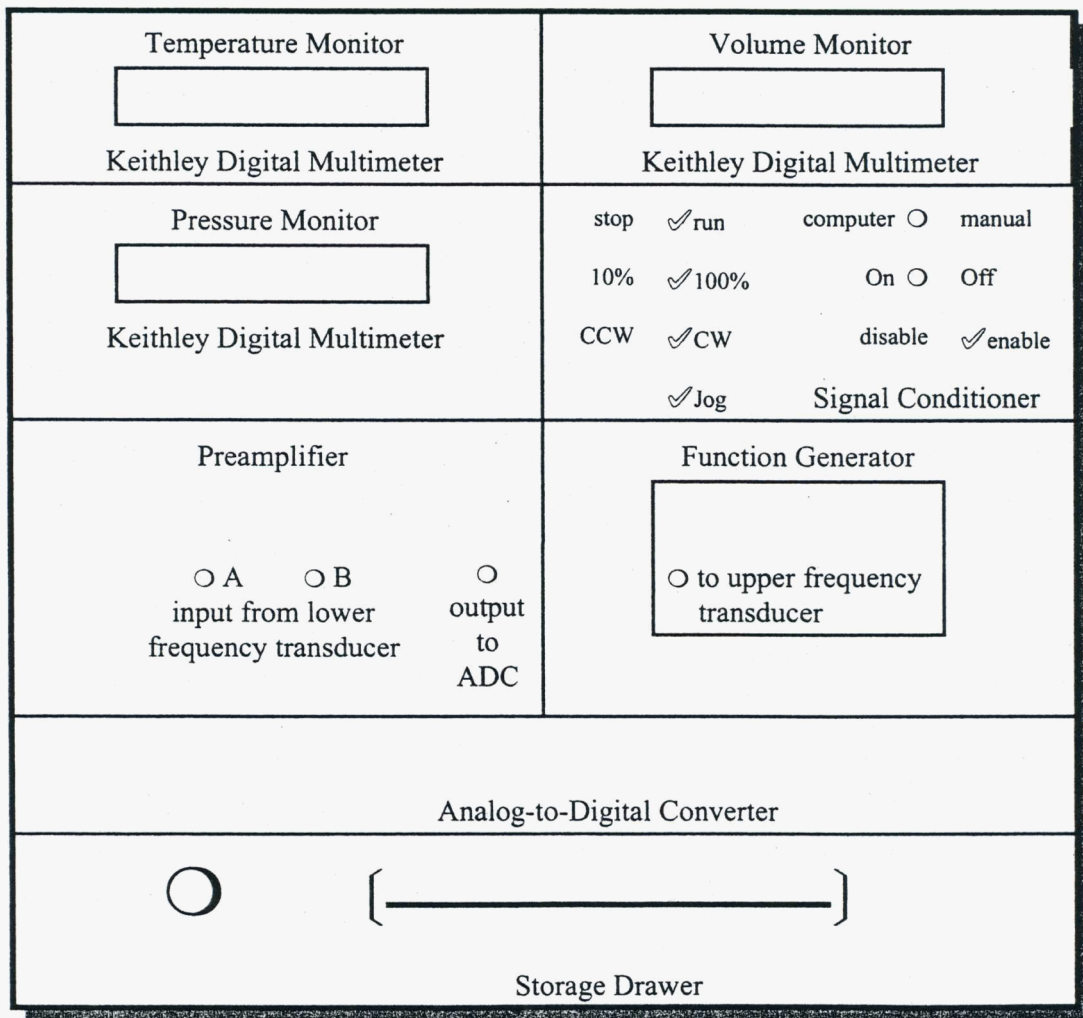
1. *Keithley Digital Multimeters.* Data acquisition equipment consists of three high resolution digital multimeters and a 16 bit, 100 kHz analog-to-digital converter. The Keithley multimeters are connected to the computer via a GPIB interface board. A digital-to-analog converter card installed in the computer provides two control setpoint signals; one is the setpoint for the oven heater, which is a 0-20 ma signal. The other is a setpoint for a liquid nitrogen proportioning valve, which is a 0-10 VDC signal. The computer parallel port (LPT1) is used to control the operation of the stepping motor that drives the volume adjustment piston and the mixing pump. The receiving devices decode the bit patterns sent from the printer parallel port.

A diagram of the ARS instrument panel is given on the following page. The digital multimeters are used to monitor pressure, volume, and temperature of the ARS cavity. Through LabVIEW the conversion of a voltage reading to SI units is time consuming compared to the data acquisition rate required for the ARS. Normally, the PVT button on the virtual display is turned off so that only ohm, amp, or volt readings are visible on the multimeters. A platinum resistance thermometer, seated within the ARS oven, is connected to the input of the upper left multimeter.

2. *Preamplifier.* Low noise electronic cables are used to connect the "A" and "B" input connectors of the preamplifier to the frequency receiver output connectors, respectively, located on the back of the control box of the oven. The wiring continues into the oven cavity, where white wires connect to two positions on the lower piezoelectric receiver. The "roll-off" setting on the preamplifier is actuated. The output port of the preamplifier goes to the ADC and then to the computer.

3. *Frequency Generator.* The lower piezodisc is not grounded; instead a floating difference of A-B signals on the frequency generator is used to compensate for background noise. Gain is set at 20, using the DC mode. A braided electronic cable takes the output of the frequency generator into the frequency input connector, located on the back of the oven. This then is connected through the oven as the input signal to the upper piezoelectric transducer. The high and low frequency band pass settings are both 6. This cuts frequencies below 10 kHz and above 30 kHz. These settings worked well at UFL but may have to be altered for the ORNL environment.

Fig. 1 ARS Instrument Panel Layout



ARS Resonant Cavity and Oven

1. *Temperature Control.* The temperature is monitored with a platinum resistance thermometer within the oven; a calibration record for the thermometer is included with ARS documentation. With the temperature setpoint at 25 °C, normal operation of the oven fans generates sufficient heat that the oven temperature will be driven to ~45 °C. Liquid nitrogen flow, controlled by a proportioning valve, is used to equilibrate and control the oven temperature to the setpoint. Control for the two channel analog output signals (0-5 V) for the oven heater and liquid nitrogen pressure valve have not be incorporated, as yet, into the ARS LabVIEW software. Two control strategies are possible for maintaining constant oven temperature:

- Below 50 °C, use the liquid nitrogen without powering the oven heater. Incorporate a PID loop into LabVIEW software to control the proportioning valve.
- Regulate nitrogen flow using a pressure valve to bleed nitrogen into the oven while the oven heater is powered. Use a control potentiostat to drive the 0-5V signal (0=close; 5=full open) of the electronic valve box seated on top of the ARS oven. Once the oven temperature is roughly adjusted, the signal from the computer (channel 2 on the DAC, hex 302 address, element 300) to the proportioning valve can be controlled through LabVIEW using oven temperature. This is the recommended option. (Room temperature might be used to control the potentiometer as an alternative to manual adjustment.)

The original temperature control for the oven was removed and replaced with a controllable rectifier using a 4-20 mA control loop. The black and yellow wires in the base of the oven connect with the DAC.

2. *Volume Control.* The volume of the cavity is determined by the piston position. A rod connects the piston to a position sensor located above the oven compartment. The signal from the position sensor is connected to the signal conditioner in the instrument panel. A 0-10 V output signal is then fed into a Keithley multimeter to display volume.

2A. Volume Calibration. A calibration of the 0.500 in ID piston position versus voltage output must be made and incorporated as input data in LabVIEW software. The following steps are needed to calibrate the piston position:

- A. Take the position sensor out of the resonance cavity and place in a lathe. Use a mil reading for sensor position and the piston diameter to accurately determine the volume of the piston for a number of sensor positions.
- B. Calibrate the pressure gauge that is mounted within the oven as a function of temperature and pressure (Use dead weights).
- C. Set the oven for a given temperature.
- D. Pressurize the cavity with 25 psi argon and seal the system.
- E. Set the piston position for small known volume (high pressure) and decrease the pressure to get pressure vs piston position ($P_1 V_1 = P_2 V_2$) to find absolute volume. (At this point the piston will have been calibrated on the basis of volume change and absolute volume.)

2B. Altering Cavity Volume. The volume of the cavity is manipulating using a stepping motor to change piston position. The stepping motor can be actuated through the computer or manually.

Computer control is the safest method of changing volume due to the safety limits built into computer programming. The stepper motor is located in back of the oven (black cylinder). The input/output lines are fed into the custom electronic signal conditioning in the instrument control panel. The computer/manual toggle enables the selection of control of the stepping motor. The stop/run toggle is used during manual control to stop/run the motor; the toggle is not actuated when the computer toggle is enabled. The Jog toggle is used to move the stepping motor by single steps. Approximately 8-10 steps corresponds to 0.1 μL volume change. (The Jog toggle is rarely used.) The CCW/CW toggle runs the stepping motor either counterclockwise or clockwise to increase or decrease cavity volume, respectively. The stepping motor can be run at 10% or 100% of full power, selected by the 10/100 toggle. (The 10% position does not currently work). A trim pot for the stepping motor is mounted on circuit board attached behind the signal conditioner front panel and is used to adjust the activation of the motor. The circuit board operates using a standard chip for stepping motors, using frequency modulation for motor control. The trim pot occasionally needs to be adjusted if the motor is not actuated when under computer control. This particular circuit board still needs a little refining; it occasionally will introduce significant noise into the volume data.

2C. Mixing Two-Phase Solutions. When the cavity solution contains two liquid phases, mixing prior to obtaining a spectra may be desired. The ARS oven is equipped with a large piston located within the base of the unit. A double-action pneumatic air valve, operated through the parallel port of the computer, controls the piston movement. A 1/16" line of pressurized air (250-500 psi head pressure) is used to actuate the valve. The resonator body is connected to the piston shaft so that the outer cavity body will reciprocate vertically while the resonator piston remains stationary during mixing. The solution will pass around and above the upper piston, before being brought down into the main portion of the resonator cavity during the off stroke of the mixing piston.

The position of the resonator piston within the cavity prior to mixing is very important.

Because the resonator piston containing the upper piezotransducer is stationary, upper and lower piezotransducers will collide if the resonator piston is set at too low a cavity volume. The cavity volume should be set at no lower than 5 mL to prevent collision. This volume should be reconfirmed during volume recalibration. The height of the short positioning posts to the right and left of the resonator cavity indicate the minimum mixing volume that can be used. If a sample volume of less than 5 mL will be used for testing, the resonator body is shaken manually by disconnecting the body from the mixing piston and manually moving it up and down.

At this point, the control of the valve has not been incorporated into the programming software. A single line of the computer parallel port will be used with a 0.1-0.2 Hz/5 sec signal. The address of the parallel port still needs to be received.

Troubleshooting: Sometimes a slight positive air pressure is required to hold down the resonator body in the well of the mixing piston.

2D. Servicing of resonance cavity. A document entitled "Procedure for Removal, Disassembly and Reassembly of PVTc Acoustic Resonator" describes how the piston assembly can be removed from the oven to replace the enclosed gaskets. This procedure will need to be performed every few experiments to prevent sample leakage from the cavity. Briefly, screws are removed where the position rod attaches to the piston, and at the base of the piston support. The transducer feedthroughs and position pins are also removed. The piston/cavity assembly is rocked to the right to lift it out of the support well. The two piston components slip out so that the O-rings can be replaced. The O-rings can be made out of PEEK, Teflon, or Hydryl. The latter is currently being used and is ordered from 2 Texaco, West Park.

3. *Pressure Control.* The pressure gauge is suspended within the oven. A 0-10V signal line is attached to the signal conditioner; the conditioner output is attached to a digital multimeter. The pressure range is 0-2000 psi; 0-15 psi is also available. A 0-500 psi gauge is currently missing from the system. Pentane is used to clean the surface of the gauge; vacuum cleaning is not usually performed. Occasionally, "Big String" is observed as the output of the pressure multimeter. This is often due to a loose electronic cable, or high background. It may be advisable under these conditions to use volume control to adjust and control pressure.

The Sensotec pressure gauge is calibrated at multiple temperatures (25, 50, 75, 125, and 150 °C) using dead weights. A curve of P_1V_1 versus P_2V_2 is then constructed to determine the relative volume change of the cavity as a function of pressure change. The absolute volume as a function of pressure can be derived by using a linear variable differential transformer with a mill bit to determine piston volume at ambient temperature and pressure.

LabVIEW programming for the ARS

1. General Description.

The general programming philosophy is based on "Do-While" logic using a single metronome to coordinate and synchronize the various input/output functions of the program. Because the GPIB board & ADC cards cannot be accessed simultaneously for each of the control tasks, all tasks are synchronized by the single clock to combine data from all transducers. Boolean case structure (primarily True-False statements) is used for each of the primary functions that must be performed. The various time devisors are 1) acoustic signal generation; 2) temperature control; 3) volume control; 4) pressure sensor signal gathering and processing; and 5) file writing. Cases 2-4 are always true; therefore the clock controls the readout for temperature, volume, and pressure at a selected clock time (375 ms is lower limit; 500-1000 ms is typical.) Programming is still needed to turn off data acquisition once the necessary number of data points has been acquired.

Since the parallel port (LPT1) is used for instrument control; a printer located on a local network must be used for hard copy. An alternative would be to install an LPT2 port on the control computer.

2. Components of art_1_15_00 VI Block Diagram

2A. Acoustic Data Acquisition Logic. Components to the far left of the block diagram set up the initial instrument values and include the logic portion of acoustic data acquisition. Data acquisition is triggered; a check for single/continuous sweep; temperature/volume sweep selection; start/stop frequencies; sweep generation rates; and signal amplification are queried using inputs from the virtual instrument panel. Events are triggered using a boolean timing loop to determine when the clock time is evenly divisible by the user-specified sampling interval. Every time data acquisition is triggered, the value of a shift register is incremented by 1 so that the sample event is numbered, and the sampling rate (sweeps/sec) can be calculated. The program is currently set up to take data at 500 ms intervals.

It takes 1.31 s to gather sweep data; maximum data frequency is 100 Hz. Resolution is equivalent to half the data frequency, therefore 50,000 Hz is the maximum frequency resolution of the system. The pick menu for the frequency span allow a selection from 5000 to 50,000 Hz. Most ARS information is best acquired at $\geq 25,000$ Hz. A pick list is also available on the panel to select the byte size used to store sample data; 131072 bytes generally provides the best resolution. The actual frequency resolution is calculated as:

Frequency resolution (Hz) = Frequency span (Hz) / sample size; the sweep time is then the inverse of this value.

The "Excitation" or sweep amplitude is controlled by the virtual dial on the panel. This dial controls the amount of sonic energy transmitted into the sample. The excitation amplitude should be run as low as possible so that the sample does not heat from excess energy dissipation. If the peaks on the time domain graph are truncated, the excitation energy is set too high.

2B. Function Generator Logic. The programming for the function generator is defined in the first large While loop that incorporates a 6-sequence case structure. The sweep and function generator are turned on (triggered) once, and then the six sequences are performed.

Seq. 0: Frequency span, sample size are defined in sequence 0; the function generator can also be deactivated.

Seq. 1: The ADC and GPIB for the function generator are set up in sequence 1. When the sweep and function generator are triggered, the ADC is simultaneously triggered to begin gathering data

Seq. 2: Data from the ADC is read as a long string variable.

Seq. 3: Sequence 3 processes the ADC data to write time domain data to the upper virtual panel graph and to form a Fourier transform array to file. This is accomplished by converting the ADC string variable to decimal format, splitting the decimal format into bytes, reversing the bytes, writing the data into integer format, and, finally, adjusting the values to fit into the frequency domain graph. The data array is squared and summed to calculate the acoustic efficiency, which is then written to the data file.

Seq. 4: After the FT data are processed, the frequency data are graphed in the lower graph box on the virtual panel. (If line noise is obvious in the FT graph, write to element 0, setting values to 0 in spreadsheet, then graph cleaned up data.)

Seq. 5: Turn off sweep and function generator.

2C. Temperature Control Logic. Temperature monitoring is controlled in the second large While loop. The upper portion of the While loop is concerned with data gathering, where data from the GPIB board is read, the data string is converted into a number, and the equation for conversion to SI temperature conversion appears. The temperature data are sent to the virtual panel's digital display and to its graph. The lower portion of the loop provides for temperature control through a potentially energized controller located in the base of the oven.

A Proportioning Integrating Differential (PID) equation is used to control the oven temperature to the temperature set point. The actual temperature is used as the input to the PID equation, output of the equation is sent to the out port (ADC) controlling the oven temperature. If the boolean loop in this lower portion is true, the driver for the temperature sweep function is set. An error value is calculated from the difference between the actual oven temperature and the set point.

The PID algorithm is structured such that:

$$\text{Controller output signal} = a \times \text{error} + b \int_{\text{time} = 0}^{\text{time now}} e \, dt + c \frac{de}{dt}$$

where "a" is the proportional constant; "b" is the integral constant; and "c" is the differential constant. Analogously, the product of $a \times \text{error}$ is the proportional component of the PID, the integrating portion follows in which $\text{time}(0)$ occurs at the beginning temperature offset, and the final PID term is the differential or "looping" component of the algorithm. The equation constants are calculated using the error function below:

$$\text{error difference} = a \left[e + \frac{1}{T} \int_{\text{time} = 0}^{\text{time}} e \, dt + T_s \frac{de}{dT} \right];$$

where "T" is temperature, "t" is time, and T_s is the relative ratios for constants "b" and "c" relative to "a".

PID equation parameters are entered in the lowest portion of the virtual panel. Before pushing the virtual ON button of the panel, the tool palette's indicator hand is used to set the PID parameters to

1000, 1, and 0 for the proportional, integrating, and derivative constants, respectively. The derivative constant is reset to a value of 1 or 2 once the panel is turned on and the graphed temperature data shows oscillation about the temperature set point. Final PID values should provide temperature control to within 0.004 °C.

The Run options for set points (SP) and pressure/volume (PV) ranges must also be selected before the panel is turned on. Values for "sp low" and "sp high" are always 0 and 100, respectively. Bit size selection for the output range are 100 for "out low" and 2048 for out high. For temperatures below 100 °C, the output high can be reduced to 1024 bites. (Need description for remaining indicator switches in options box.)

2D. Volume Control Logic. The third While loop programs volume control of the piston. The loop contains a read request for the temperature multimeter, the volume calibration equation, readout to the digital indicator on the control panel and parallel port output (hex 378), the bit pattern to drive the piston to next incremental volume, an analog conversion of the temperature sweep; and write capability to the multimeter screen for SI units.

2E. Pressure Control Logic. Data acquisition and control of pressure is accomplished in the fourth While loop. Imbedded in this structure is a boolean loop to write output of the pressure transducer to the multimeter (PS1); read the GPIB board and take the output to the ADC; convert the reading to SI units if desired; write the pressure to the digital indicator on the virtual panel; continuously graph the pressure; and, finally, a logic loop to plot the acoustic efficiency panel graph and update its corresponding digital indicator once the experimental sweep is complete. (An indicator should be added to the virtual panel to warn of excess pressure build-up during the oven warming cycle.)

2F. Data Storage and Retrieval Logic. The final While loop handles data storage to disk. The time, acoustic efficiency, temperature, volume and pressure are written as an ASCII array. The operator supplies a file name and path on the virtual panel. The time domain and element number in the sweep are written as a binary file to disk.

ARS Instrument Operating Notes

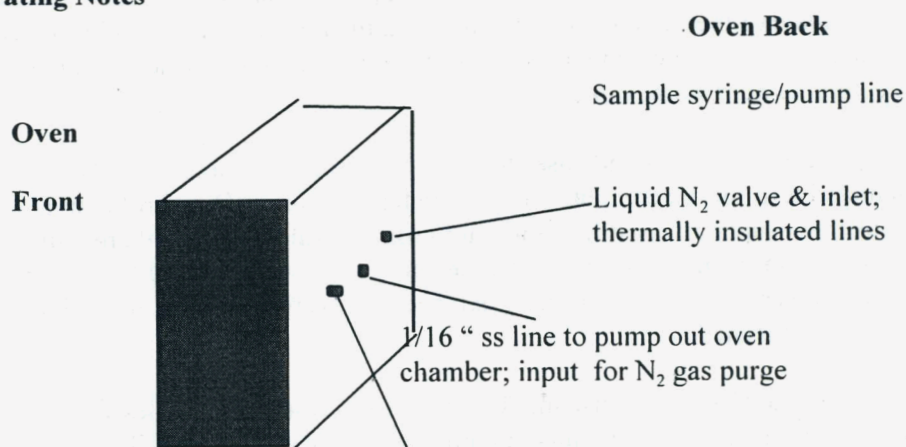


Fig. 2 Exterior connections to the oven cavity

1. Exterior flow connectors to the oven (Fig. 2) include a 1/16" stainless steel sample line that can be filled or emptied using a syringe or pump. A 1/4" line connected to a proportional valve controlling liquid nitrogen flow from a dewar is attached to the middle back of the oven. Finally, 1/16" stainless steel tubing allows gas flow from bottled inert gas. Flow lines within the oven chamber are shown in Fig. 3. These include sample lines leading into the piston chamber, gas purge line
2. The ARS system and sample are prepared for use by first degassing the liquid sample under vacuum. The oven door is closed; all transfer lines and the oven interior are purged with nitrogen gas. An oil or rotary pump is used to reduce the oven chamber pressure to 10^{-3} torr overnight. A cold trap on the pump line is used to condense trapped gases.
3. LabVIEW programming is accessed by turning on the computer; selecting START and entering ORNL as the user and as the password. Double click on the LabVIEW icon; the response should be LabVIEW 5.1. Select OPEN VI, then art_1_15_00 (or the most recent version of art). The virtual control panel for the ARS should be brought up on the screen.
4. Set the PID parameters values located on the lower left of the panel, using the indicating hand of the tool palette.
5. Sample Introduction Safety precautions:

To protect the ARS cavity and transducers from over-pressurization, enough head room within the cavity must be left to allow for vaporization of the sample during oven heating. The zero volume state is when the piston is completely down in the cavity. To introduce the sample, open the sample valve and supply pressure from the sample syringe or pump while increasing the cavity volume until no more than 5 mL of sample is transferred into the cavity. Maintain a small positive pressure on the sample so that the sample does not separate. Close off the sample valve and reposition the piston so that the interior volume of the cavity greater than 0.5-1 mL of the sample volume originally introduced. This additional volume will allow for sample expansion without high pressure while the sample is heating. Enter the value for the total volume to the "Start Point" volume indicator on the control panel. Once the operating temperature is reached and there is no chance of a pressure spike, the "start" volume can be re-entered as the actual volume of the sample only. In so doing, the piston position will reset to sample volume. Set the "tolerance" value on the panel to 0.00050 so that the piston position is controlled to within 0.00050 μ L of the volume Start Point value.

If the cavity pressure increases too abruptly during heating, open the oven door to rapidly cool the system and turn off the computer so that the temperature PID control loop is cut off. If the computer power flickers or turns off, or if the computer programming locks up, there will be no control of oven heating. The temperature limit for the piezoelectric transducers is 150 °C. Therefore, immediately turn off the oven power to prevent transducer damage and over-pressurization until computer control of the system can be reinstated.

6. Click the virtual ON button; use the Run bar (\Rightarrow) to reset the Keithley multimeters. These will be operating in the read mode, with units in ohms, volts, and current. While the ARS system is equilibrating, readout can be converted to SI units by selecting the PVT display button located below the ON button of the display panel. This can also be done by bringing up the LabVIEW diagram window, then acquiring the tool palette, followed by selecting the probe tool. Click on the output line of the temperature, pressure, or volume conversion sequence within the respective program cases to view the SI output. Approximately 2 h is required to reach temperature equilibration; look on the Control Temperature scan of the virtual panel to determine when the ARS system is at equilibrium.

7. Virtual Panel Set Prior to a Sample Run

7A. *Frequency/Sampling Entry Box*. Set the values for the following functions:

Function	Typical Setting
Frequency Span (Hz)	25,000 or 50,000
Sample Size (Bytes) for data storage	131072
Excitation Amplitude	2
Continuous/Single sweep	Continuous

7B. *Sweep Entry Box*. Select between a temperature or volume sweep. Enter the Current Set Point (starting point for sweep), Sweep End Point, and Number of Points to be taken in the sweep. The sweep increment size will thus be:

$$\text{sweep step size} = \frac{|\text{set point} - \text{end point}|}{\text{number of points in sweep}}$$

The number of points selected for a scan is dictated by the storage media for the Fourier transform of the sweep data (1.3 Mb for floppy). Approximately 0.25 Mb of storage room is required per point in the time domain; the FT data will need twice this amount of storage space.

The Point Freq is the interval size that the frequency data is collected throughout the frequency span. Usually a run is set up to last about 15 minutes. For this to occur, the Point Freq must be set at the appropriate interval. For instance, in a 1000 point run at 50,000 Hz frequency span, the time between points would be 900s/1000 point or 0.9 s and each point frequency interval would be (50,000 Hz)/(0.9 s) or 55,000 Hz. In entering a value for Point Freq, remember to take into account that time for the run must be selected to ensure that the sample has come to equilibrium after each volume/temperature change.

The path and file name for final data storage to floppy or hard drive must be entered in the PVTc Path and File box. The button to the right of the box is pushed when data is to be saved. All sweep values in the Sweep Entry Box must be entered before data is stored. Data is stored in the sequence: "time," acoustic efficiency, temperature, volume, and pressure. Once the ARS set points have been reached to assure system equilibrium, the data storage file is pushed on, then off, to acquire baseline data. If data acquisition is in progress, and the data stored thus far must be accessed, do not open the VI from Windows Explore. This will crash the system and shut down computer control of oven temperature. Instead, copy the file to a floppy and open the copy by using Excel under text format. Locate the test name and time.

The Time Domain button queries for taking time domain data rather than frequency data; the Start Sweep is then pushed to begin data acquisition. As each scan is made, a new Time Domain graph is plotted and the volume (or temperature indicator) box is updated. A scan can be stopped by pushing again the Start Sweep button, and then restarting the scan. If the Off button of the virtual panel is used instead, previous data will be lost and the oven temperature will not be controlled.

Push the Time Domain and Start Sweep buttons when all sweeps are completed. Push the PVTc off to quit storing data. Currently the sweep count is compared to the Set (scan) number in the program to turn off incremental volume/temperature changes. However, data is still collected beyond the final set point until the PVTc button is turned off.

8. Temperature, Pressure, and Volume Box

Each of the above parameters has an indicator box at the upper left of their respective graphs that gives the current ARS cavity values. The Start Point for temperature and volume must be entered using the indicator hand of the Tool palette. The output of the PID equation is continuously updated in the PID Output indicator box associated with temperature data. The value for acoustic efficiency is updated in the Efficiency indicator box; acoustic efficiency can be graphed as a function of time by shifting the virtual switch toward Efficiency. The degree to which the cavity volume will be controlled is set in the Tolerance box associated with volume data. Typical volume tolerance is 0.0005 mL.

9. Data Retrieval

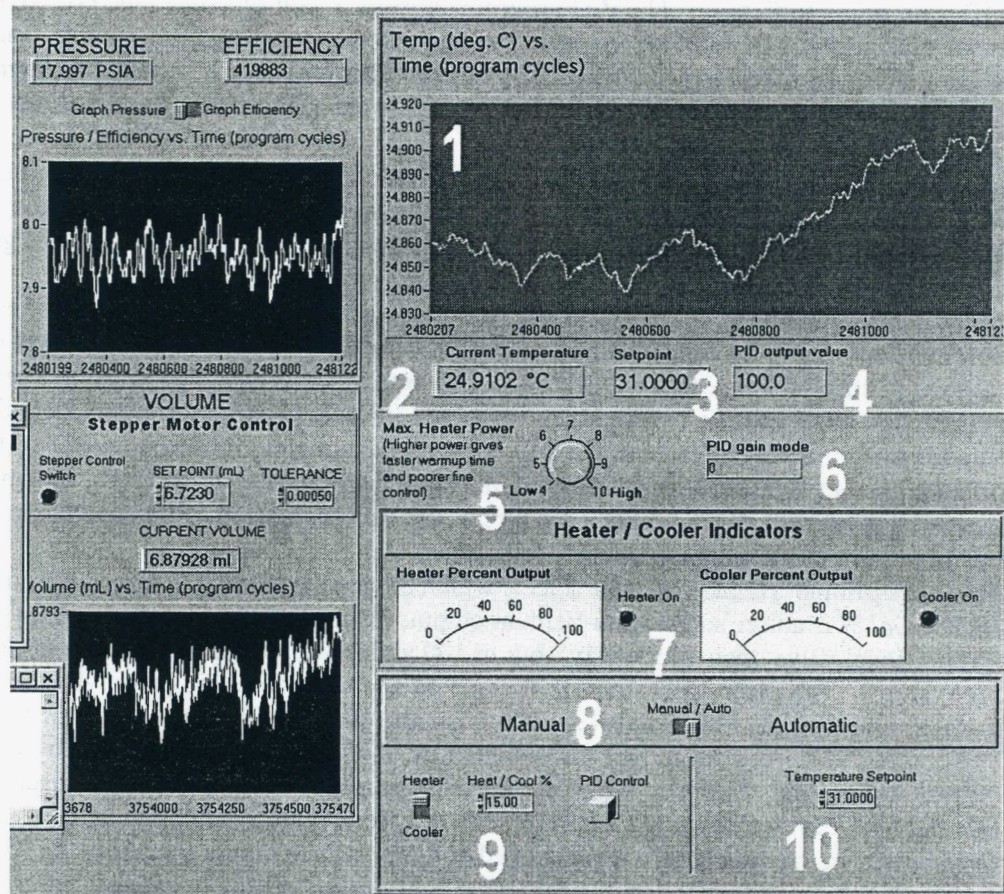
- A. Open VI file under Excel using text (.txt) format
- B. Insert a column with the following equation $(a1-\$a\$1)/1000$ to get true time since approximately 1s is required to transfer digital voltmeter data.
- C. Plot acoustic efficiency vs pressure.

10. Instrument Shut Down

If the scan was run at sub-ambient temperature, watch that the pressure does not increase significantly as the system is brought up to room temperature. Flush the cavity with solvent; turn off the power to the oven and pumps. Back out the piston position to 6-7 mL volume (total piston volume = 8 mL). Turn off power strips to ARS instrument console and computer.

**APPENDIX B:
OPERATING INSTRUCTIONS FOR THE ACOUSTIC
CAVITY RESONANCE SPECTROMETER**

C. A. Willis
August 6, 2001



1. **Temp vs. Time chart** shows the temperature in degrees Celsius versus the number of iterations the program loop has executed. After the program has been running awhile, the chart displays an interval of approximately 12 minutes. Generally, unless the acoustic signal is being processed on every iteration (continuous scan mode), there are about 1.4 iterations per second.
2. **Current Temperature:** the latest measured temperature
3. **Setpoint:** indicated setpoint only; set the setpoint at the bottom of the panel.
4. **PID output value:** number between -100 and 100 that controls heater or cooler output. A negative number means the PID will attempt to cool the oven; positive means the PID will heat the oven. The PID value is shown whether or not the PID is actually engaged in controlling (i. e., even in manual mode the current PID value will be calculated and displayed, just not sent to the temperature control devices).
5. **Max Heater Power:** determines the heater power range that can be used by either the automatic or manual control options. In the default 10 setting, maximum heater power is full 120-volt power to the elements. At the 5 setting, only half as much of full power is allowed. Since this input affects the heating time of the oven, it has a substantial influence on the behavior of the PID control, and should be chiefly used to help tune the PID. The recommended setting, for full power range and fast heating, is 10. In general operation of the ARS, this control should be left alone. To manually control heater output, use the *heat %* setting under "manual."

6. **PID gain mode indicator:** The PID program consults a gain schedule (see bottom of panel) that depends on setpoint temperature and current error from the setpoint. Gain mode shows which PID gains are currently in use. This indicator is mainly for diagnostic purposes. To find the actual gains that correspond to the Gain Mode, go to the PID controller box at the bottom of the screen.
7. **Heater / cooler indicators** display the current heater or cooler output, either from the PID or from a manual setting. Both heat and cool cannot be running simultaneously. The red LED means the heater output value is being sent to the oven control. The green LED means the nitrogen proportional valve is being regulated by the output.
8. **Manual / Auto switch:** In manual mode, you can do the following: set heater or cooler power from 0-100% by hand, OR engage the PID controller directly with any level of setpoint /measured temperature difference. The auto mode is designed to get to a setpoint temperature automatically as quickly as possible. In cases of large difference between setpoint and current temperature, the PID is bypassed and either 100% or ~ 60% of heater or cooler power is automatically selected, depending on the size of the error. When measured temperature gets within 1.5 degrees, the PID is engaged. PID control alone would require much longer to get to a setpoint.
9. **Manual options:** *Heater / Cooler* selects which device the manual power value controls. *Heat / cool %* is a user setpoint for percent output, from 0-100%. For 100% cooling (proportional valve open all the way), put in 100 and move the selector switch to Cooler, for example. The green LED above will come on and the Cooler indicator will show 100. Turn on (push in) the *PID Control* switch to use the current PID values to control heating and cooling. The setpoint for the PID is under the Automatic heading (see below).
10. **Automatic option:** *Setpoint*. This user input is the temperature at which the user would like the ARS cavity to be held. It can be set to any temperature, although certain components in the system will be destroyed at temperatures higher than 150 deg. C. Temperatures lower than 0 deg. C necessitate first turning off the oven (red switch on front of oven) to keep water condensation from shorting live electrical connections. The control system currently works well in the range of 20-120 deg. C, though low temperatures can take a while to reach with good stability because the cooling scheme is inefficient.
11. **PID Controls Box** (Below the Temperature Controls Box, not shown on above image). User inputs to determine the behavior of the PID program, ordinarily set at default settings and left alone. *Integration Non-linearity* multiplies the raw integral (I) term of the PID output by a non-linear scaling factor to prevent integrator windup (and loss of control). Highly recommended (push button in to turn on.) If ON, user can use the switch to the right to set the scaling factor proportional to $1/\text{error}$ or $(1/\text{error})^2$ (default). Having *Integration Non-linearity* turned on means one cannot apply the Zeigler-Nichols method or other empirical equations for tuning the PID and expect good results. The gain schedule in place for default PID operation was experimentally determined and best fits the $(1/\text{error})^2$ scenario. *Gain Scheduling:* the only important control in this box is the *PID Parameters* array input. In the lefthand corner, choose the number of the gain schedule to be revised, or to be entered for the first time. *Kc* is a scaling factor for all terms (P, I, and D). *Ti* is the integral term time constant- the time averaged (integrated) error is multiplied by Kc / Ti . *Td* is the differential term time constant- the derivative of error with respect to time is multiplied by $Kc * Td$. Use the default values for assured good performance over the 20-120 deg. C range. *PID Options* should be left alone at default values for normal operation.
12. **Heat / Cool Crossover Temp.** (Not shown on above image- it is below the Temperature Controls Box and to the left.) This user input selects at what temperature the program will change from heating mode to cooling mode when under PID control. To minimize

hysteresis and runaway situations, the PID only controls either the heater or the cooler when it is engaged in auto or manual mode. Below the crossover temperature, the PID only operates the cooler. At or above the crossover temperature, the PID only operates the heater. This value is best set to the maximum temperature the oven reaches when sitting idle with the blower on, which is about 52 deg. C. Unless, of course, the user wishes to input 52 deg. C as a temperature setpoint to hold over long periods of time, in which case the crossover temperature input should be adjusted up or down a degree or two.

Programming description: the most recent version of the ARS LabVIEW control is called **ARS.VI**, which is accompanied in the *C:\CarlVI* folder by the **temperature.llb** library. All the files created or modified by Carl Willis are stored in this library. Other files are in the LabVIEW libraries.

The temperature control subVI is called **tempcon.VI**, in **temperature.llb**. This large file utilizes 1) the PID algorithm, called **schPID.VI**; 2) the gain schedule selector and setpoint change manager, **spchange.VI**; 3) the oven heater driver, **heat.VI**; and 4) the nitrogen proportional valve driver, **cool.VI**. For every iteration of the CarlVI control program, **tempcon.VI** runs once. First, cavity temperature is measured and converted to deg. C by a formula node with the thermometer calibration equation. A case structure with *cases 0, 1, 2, 3, 5 and 9* runs, with the following consequences: *case 0* is executed if temperature lies between 1.5 and -1.5 degrees from the setpoint, AND automatic mode is selected. *Case 0* allows the output from **schPID.VI** to control **heat.VI** or **cool.VI**, depending on whether the subordinate true-false case is true or false, respectively. This true-false case is decided by whether the temperature is above or below the heat / cool crossover temperature. If the cool (false) option is in effect, the PID output value is negated- **cool.VI** only accepts a negative input. *Case 1* occurs if temperature is low by no more than 6 deg. C from the setpoint. A pre-chosen signal (60-90%) is sent to **heat.VI**. Since the oven requires more power for a given rate of temperature increase at higher temperatures, the exact value of the output signal (60%, 75%, 90%) depends on whether temperature is less than 60 deg. C, between 60 and 90 deg. C, or greater than 90 deg. C, respectively. *Case 2* occurs if the manual button is selected on the front panel. If the manual-mode PID switch is ON, the PID output is sent (as in *Case 0*) to **heat.VI** or **cool.VI**. Otherwise, the user's 0-100% and heat / cool selection are sent. *Case 3* is active if automatic mode is set and the temperature is more than 6 deg. C colder than setpoint. In this case the heater is activated at 100% capacity. *Case 5* occurs if automatic mode is set and the temperature is between 1.5 and 6 degrees warmer than the setpoint. A 50% cooling signal is sent to **cool.VI**. *Case 9* executes if automatic mode is set and the temperature is more than 6 degrees warmer than the setpoint. A 100% cooling signal is sent to **cool.VI**. At the left side of the screen in the **tempcon.VI** diagram are **schPID.VI** and **spchange.VI**. In order to supply gains to the PID program, the current setpoint temperature is sorted into one of four "bins" depending on whether it lies 1) below 30 degrees, 2) between 30 and 70 degrees, 3) between 70 and 95 degrees, and 4) above 95 degrees. In each such category, there are two subcategories: one for a high setpoint-process variable error and one for a low (below 0.05 deg. C) error. The gain schedule selected by the lower error value has a larger proportion of differential action in each situation. The chosen gain schedule reference number is sent to the *scheduling variable* input on **schPID.VI**.

SchPID.VI is the PID controller VI. Inputs to the VI are a *process variable* (measured temperature in this case), a *setpoint*, a clock (in the form of the **ARS.VI** iteration count), a *scheduling variable* that dictates which entry in the gain schedule is used, and clusters that are accessed on the front panel of **ARS.VI** to provide the gain schedule and various other PID options. First in this program, subVI **PIDparameters.VI** executes, extracting the PID gains from the gain schedule according to the number supplied at *scheduling variable*. Input *process variable* is low-pass filtered (by averaging it over several iterations); error, which is the

difference between *setpoint* and *process variable*, is calculated; proportional, differential and integral response are all calculated by their respective subVIs and are multiplied in those subVIs by the appropriate gains; the results are all added and scaled to produce the final output. The *manual control* option is not used at all here. (Manual control on the front panel of **ARS.VI** is a totally independent action, carried out in **tempcon.VI** directly.)

Spchange.VI is actually quite an involved little program, designed to effect "bumpless" transition at a sudden change in setpoint, such as when the user changes the *setpoint* control while the **ARS.VI** program is running. This program determines whether to use the high- or low-differential-action gains (see **tempcon.VI** description above) by checking if temperature error is greater or less than 0.05 deg. C in magnitude. The orange shift register stores last iteration's value of the setpoint. First, this is compared with the current value of the setpoint. If last run's value is equal to this run's value (meaning nobody changed the setpoint), AND the error is 0.05 deg. C or less in magnitude, the outer case structure will be *TRUE*, enabling a high output to the "gain sch. select" terminal. But if last iteration's setpoint was different, OR if temperature error has gotten larger than 0.05 deg. C in magnitude, the outer case structure is *FALSE*, and 0 will be sent to the *gain sch. select* terminal. In the *TRUE* case, there are two possibilities, represented by the inner case structure. If output to the gain scheduler was 0 in the last iteration (stored in the green shift register), the inner case will be *FALSE*, and the output to *gain sch. select* will be low for 1000 ms before going high. This gives the PID a chance to adjust to the new gain schedule or new setpoint before enabling the high-differential-action gain. If this were not done, the setpoint change would be amplified by the high differential gain and a runaway would ensue. After the 1000 ms timer has finished, a high output is sent.

Heat.VI is simple and, for the most part, self-explanatory. The one fine point worth noting is that the output to port 768 (a 4-20 mA output from the DAC card in the computer) is not linear with respect to the heater signal input, but is rather proportional to the square root of the input signal. This is because the oven heater power control in the oven is effectively a linear current amplifier, much like a transistor. Current through the device and heater elements in series is proportional to the current in the 4-20 mA control signal. But thermal power given to the oven is the same as the joule losses in the heater elements, which are proportional not to the current but to current squared ($P = I^2 R$). Thus the square-root gives a much more linear signal-to-oven-power relationship. The 625000 multiplicative factor scales the 0-100% input value to give up to 20 mA output from the DAC card.

Cool.VI is a much more involved program than **heat.VI**, the principal reason for which is regulating the momentum of the proportional valve drive shaft so as not to slam-lock the valve closed or open. The output cold signal is a 0-10 VDC output from the DAC card, controlled at port 302 (hex). Within the while loop at the center of the diagram is a routine for displacing the valve in increments so that angular momentum doesn't get out of hand. Output is proportional to input for the cooling valve.

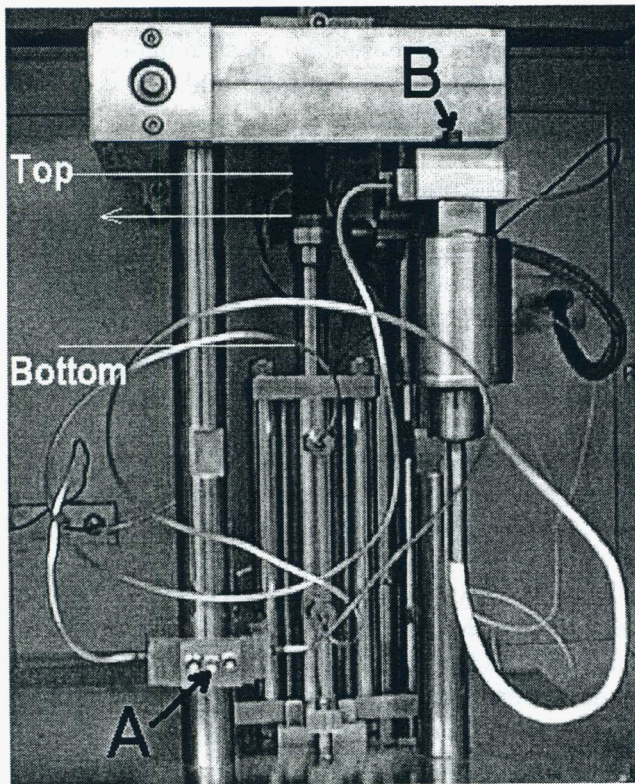


Fig. 2 Positions of filling (A) and exhausting (B) valves. The exhausting valve is in the line to the vacuum system. The filling valve is in the line to the injection port in the rear of the ARS. Also shown are the approximate range limits (top, cavity max volume; bottom, min volume) and the current piston position (arrow).

Loading or Unloading a Sample in the Cavity: refer to Figure 2 above. There are two needle valves mounted in the oven chamber, near the cavity. They both have an Allen (hexagonal) head on the needle valve screws, and they would be scarcely recognizable as valves unless you note the stainless steel tubing going to each one. **Valve A** is the filling valve, opening the sample reservoir to the ARS cavity. The valve opens by turning the needle screw to the left with an allen wrench. **Valve B** is the evacuation valve, mounted over the pressure transducer (the transducer is always open to the cavity). It takes a different, slightly larger allen wrench than the filling valve. The needle screw faces the oven ceiling and can be difficult to turn. This valve also has leakage problems unless it's really tightened up. The leak is largest to the cavity side of the valve.

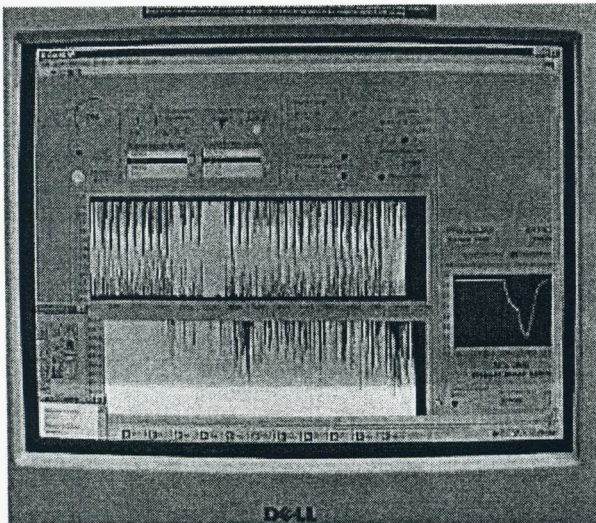


Fig. 3 A noisy signal characteristic of stepper motor vibration. This problem is especially noticeable in the FFT.

Stepper Motor Noise: the stepper motor makes acoustic noise that can swamp the normal signal. Over some PVT ranges, this problem is not significant, but most of the time, it needs to be prevented. Figure 3 shows what motor noise looks like.

Proportional Valve Jamming: although the incremental-displacement method of cool.VI is very successful in mitigating the jamming problem, it can still happen when the valve is driven all the way shut or open very quickly. Signs of this problem are a failure to regulate temperature to a setpoint below 52 deg. C. The motor on the valve gets extremely hot also, and the metal parts on the axle of the valve get too hot to touch. It is best to periodically check for this problem when using the cooler, by feeling the valve motor. In case of a jam, smoothly but forcefully rotate the axle of the motor with pliers. Either grab the brass coupling between motor and potentiometer, or the brass collet clamp between the motor and the drive screw. Don't remove power to the valve- thus, when the valve is un-locked, it will advance to its correct position as a sign that it is working. The motor axle should always be easy to rotate by hand over about half a turn.

Frozen Oven Blower: after having had the ARS very cold, less than 0 deg. C with the oven power off, do not attempt to restart the oven until condensation has melted and evaporated from the motor. Ice buildup will lock the motor axle, and water in the motor windings could be very destructive. The oven, if suffering from condensation in the motor and fan, will make a loud 60-hz humming noise but will blow no air. Or, the motor and fan may come on, but with a loud banging and scraping sound as ice is tossed about in the fan housing.

Cavity piston position: it is important to know what the cavity looks like with the piston in and out. It is especially important to note when the piston is dangerously close to crushing the transducers at its low volume end (see Figure 2). Never leave the stepper motor running in the clockwise direction (decreasing volume) without careful observation. Sometimes, when volume is being increased in the cavity, the piston will drag the whole cavity assembly up with it. In this situation, simply use a hand on each side of the cavity and forcefully push it back to the bottom of the oven. Sometimes some leverage is required, achieved by putting a wrench handle between the piston-driver coupling and the top of the cavity assembly. When not under computer control and not being actively used in manual mode, turn the stepper motor off with the red panel switch on the signal conditioner, marked *stepping motor*. It seems that the motor gets very hot when just left on. Whether or not this is a particularly bad condition is not known.

APPENDIX C
PROJECT STATEMENT

PROJECT STATEMENT

Name: GAVRILIUC IONEL ROBERT
Country: ROMANIA
Project title: DIMETHYL-ETHER - THERMODYNAMIC RESEARCH

Background

The thermodynamic and thermo-physical properties of dimethyl-ether ($\text{CH}_3\text{-O-CH}_3$), as well as the fact that it is harmless to the ozone layer, recommend it as a possible substitute substance in refrigeration, as propellant for sprays, and as possible fuel for the Diesel engines too. Knowing its properties is extremely important for the engineering use of this substance.

The study of the thermodynamic and physical properties for dimethyl-ether has revealed great differences, regarding especially the critical parameters. It is on these critical parameters that the equation of state is based on. Such an equation is presented by Rudolf Plank, and the authors of the REFPROP 5.0 program use such an equation for computing the thermodynamic properties of the refrigerants they are dealing with.

Under these circumstances, the following question is fully justified: "How precisely have the critical data—along with all the other measurable properties of this substance—been measured?" Another reason for performing such experiments is that the published experimental data for dimethyl-ether are very scarce.

Objectives

During this project, I intend to perform experiments regarding measurements of the following properties of dimethyl-ether:

- c_p – specific heat capacity at constant pressure;
- c_v - specific heat capacity at constant volume;
- the Joule-Thompson coefficient.

Methodology

Knowing the thermodynamic properties of a substance used in the energy technique is a necessary condition for being able to think upon such energy processes. This relation becomes obvious when we speak about using environmentally friendly refrigerants as drop-in substances for CFCs in the refrigeration machines.

During a thermodynamic state, change of real gases through adiabatic throttling, the enthalpy before and after throttling, has the same value, and it can be best observed in a h - s diagram or a T - s diagram having curves of constant enthalpy. The throttling process—as irreversible process—takes place only with entropy increase. The wet vapours get cooler and thus their quality increases. Only when the throttling process takes place near the critical point, the vapours become at first wetter.

One can see this process better in a h - s diagram, where the curves of constant enthalpy are horizontal. If saturated vapour is being throttled, the temperature

decreases in the neighbourhood of the saturation curve (the way shown by the curves of constant temperature in the superheated domain). The temperature decrease is greater when the initial pressure is bigger. If the process takes place further away from the saturation curve, finally the temperature remains constant, according to the asymptotic look of the curves of constant temperature (which become closer to the horizontal).

If saturated or superheated vapours get throttled in the neighbourhood and above the critical point, the cooling effect of throttling—known as the Joule-Thompson effect—can be better observed. Linde has first used this phenomenon for producing liquid air. In case of ideal gases, the temperature remains constant during throttling. The Joule-Thompson effect is thus a measure of the deviation of real gases from the ideal state, and it reveals the basis for building up the caloric equation of state for vapours.

By throttling, one can find out the liquid content of wet vapours. The wet vapours are flown through a so-called throttling calorimeter (which has to be very well insulated), and the pressure decreases so much that the vapours get superheated. If pressure and temperature is now being measured, the state point can be easily placed on a h - s diagram in the superheated domain. Starting from this point, one can only go horizontally in the wet vapours domain, and can read the starting quality on the “ $x = \text{constant}$ ” curves. It is also possible to compute the quality x , knowing that the enthalpy h of the superheated vapours is: $h = h' + x r$, and thus the vapour quality x is: $x = (h - h') / r$.

The enthalpy can be established (in most cases) by measuring the temperature increase that occurs when heating electrically (at constant pressure) a flowing flux of vapour through a calorimeter. The heat transferred to the vapours is equal to the enthalpy increase, and one can get the specific heat capacity by dividing it through the temperature difference:

$$c_p = \left(\frac{dh}{dT} \right)_p$$

The throttling effect can also be used for enthalpy measurements. If vapours are being expanded in a throttling calorimeter (well insulated from the surroundings) by a small value Δp , the temperature decrease at constant enthalpy is:

$$\Delta T = \left(\frac{dT}{dp} \right)_h \Delta p$$

and this is called the Joule-Thomson effect (which can be measured). The experiment leads to the differential $(dT/dp)_h$, that is the slope of the curve $h = \text{constant}$ in a p - T diagram. If this procedure is used for many state points, through integration one can get the whole group of curves of constant enthalpy.

Even more favourable from an experimental point of view is the isothermal throttling, which occurs when so much heat is transferred to the vapours during the throttling process that no temperature decrease happens. The heat transferred in such a case is $(dh/dp)_T \Delta p$, and the experiment produces the differential $(dh/dp)_T$, that is

the slope of the isothermal curves in the h-p diagram. The integration leads then to the curves of constant temperature.

Significance

The project, "Dimethyl-ether-thermodynamic research," is important because it can provide experimental data on which theoretical assumptions can be very well founded. The literature survey revealed that there are very few (if any!) experimental data on this substance. The only tabular data available are those from Rudolf Planck's "Handbook of refrigeration" (dated 1956), so they are about half a century old!

The project is also extremely interesting for myself because it goes to the "bottom" of thermodynamics and also shows the way the thermodynamic diagrams are built. The engineers use lots of diagrams many times, without asking themselves how they were made—the project is the answer for it.

The project is supposed to provide a set of reliable experimental data, which are of great importance for the specialists from the chemical and refrigeration industry, not only from my own country (like the ZECASIN Company), but also from elsewhere in the world.

Evaluation and Dissemination

The results of the research will be gathered in a final report, which will be available for all the possible interested specialists. These results will also be added to the data banks dealing with chemical substances, and (possibly) placed on the Web. The Romanian ZECASIN Company will have access to this information too.

Justification for Residence in the United States for the Proposed Project

In the United States there are special organisms dealing with acquiring physical data on substances, like the Oak Ridge National Laboratory and the National Institute for Standards and Technology. They are provided with thermodynamic equipment of high accuracy, they have extremely well trained people, with lots of tradition and experience in this kind of a job. Even some temperature transducers from the lab in Karlsruhe (Germany) where I worked, were calibrated at laboratories in the United States, so that the American laboratories are real standards in this business.

Duration

The project is supposed to be completed in 10 months, according to the following timetable:

- **Month 1 to 3**

Getting acquainted with the measuring devices in the lab.

Procurement of the substance for the experiments, test of its purity.

Theoretical training in the field of numerical treatment of experimental data.

- **Month 4 to 5**

Experimental work by performing measurements of the c_p , c_v and Joule-Thompson coefficient for dimethyl-ether. The data will be gathered with a

“Data Acquisition System.” The domain for temperature and pressure data shall be the one used in most of the refrigeration and heat pump devices. The small temperature and pressure paces need a lot of work to be done, but the result will be consistent tables or diagrams for engineering use.

- Month 6

Evaluation and processing of the experimental data in order to obtain the heat capacities c_p and c_v , and the Joule-Thompson coefficient. Processing the data for obtaining an equation of state for dimethyl-ether. This equation of state is very important because all the thermodynamic properties can be computed (by differentiation) out of this equation.

- Month 7

Graphical presentation of the diagrams built on the basis of the experimental data gathered during the research, by means of computer aided graphic design.

- Month 8 to 9

Experiments with dimethyl-ether in an already existing refrigeration machine and measurement of the process properties for different functioning conditions. Building a computer program for the simulation of the compression refrigeration process.

- Month 10

Writing the final report on the research topic.

English Proficiency

I am a testified translator from English in Romanian, for the technical domain (certificate No. 127 / 1997). I have been learning and speaking English for about 30 years. From my own point of view—considering myself as a foreigner who hasn't lived for long periods of time in English-speaking countries, I consider my proficiency in English as excellent, in speaking, reading, and writing.

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